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# **How a Small Modification of the Corona-Forming Block Redirects the Self-Assembly of Crystalline-Coil Block Copolymers in Solution**

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## ABSTRACT

In this study we examine how the self-assembly of crystalline-coil block copolymers in solution can be influenced by small changes in the chemical structure of the corona-forming block. Three samples of polyferrocenyldimethylsilane-*block*-poly(2-vinyl pyridine) that form long fiber-like micelles uniform in width in 2-propanol, were treated with methyl iodide to convert a small fraction (0.1% to 6%) of the pyridines to methylpyridinium groups. When these partially quaternized samples (PFS-*b*-P2VP<sup>Q</sup>) were subjected to the same self-assembly protocol, very different structures were obtained. For PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q</sup>, the presence of positive charges led to the formation of much shorter rod-like micelles. In contrast, for PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q</sup> and PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q</sup>, complex platelet structures were obtained. We explain the complexity of these structures in terms of a distribution of compositions, in which the polymer chains with the highest extent of methylation are the least soluble in 2-PrOH and the first to associate, leading to two-dimensional aggregates. The less quaternized polymer chains remaining in solution have a stronger tendency to form elongated fiber-like micelles that grow from the ends of the initially formed planar structures. In this way, we show that small extents of chemical modification of the corona forming chains can modify the self-assembly process, and that simple one-pot protocols can lead to diverse hierarchical structures.

## INTRODUCTION

The self-assembly of amphiphilic block copolymers in selective solvents has been of interest for more than half a century, from both a structural and application point of view.<sup>1,2</sup> Recent reviews on this topic show a continuing strong activity in this field.<sup>3</sup> While most of this activity has focused on coil-coil block copolymers that form micelles with an amorphous insoluble polymer core surrounded by a solvent-swollen corona, special features are associated with crystalline-coil block copolymers that can form micelles with a semicrystalline core.<sup>4-6</sup> Crystallinity tends to promote formation of morphologies characterized by low curvature.<sup>5-7</sup> We have used the term “crystallization-driven self-assembly” (CDSA) to describe cases where crystallization of the core-forming block drives the self-assembly process.<sup>8</sup> The earliest examples were poly(ethylene glycol)-*block*-polystyrene (PEO-*b*-PS) diblock copolymers that formed planar PEO single crystals in solvents selective for PS.<sup>6,9,10</sup> The first rod-like micelles reported involved poly(ferrocenyldimethylsilane) (PFS) block copolymers.<sup>11-13</sup> Other more recent examples of rod-like micelles involve block copolymers with polyethylene (PE),<sup>7,14-20</sup> polyacrylonitrile (PAN),<sup>21</sup> polyferrocenyldimethylgermane (PFG),<sup>22</sup> poly( $\epsilon$ -caprolactone) (PCL),<sup>23-30</sup> poly(L-lactide) (PLLA),<sup>31-35</sup> and polythiophene,<sup>36,37</sup> as the crystalline core-forming block. Some of these materials tend to give mixed morphologies, such as the coexistence of rods and spheres.<sup>28,38,39</sup>

From a theoretical perspective,<sup>40</sup> micelle morphology represents a balance between the energy of crystallization that promotes the formation of a folded lamellar core, and the interaction energy of the solvent-swollen corona chains. To minimize strong corona chain repulsion, core-forming chains of a block copolymer can form a thinner core with a larger number of folds to increase the distance between the anchor points of the corona chains. When corona chain

repulsion is sufficiently strong, crystal growth in the lamellar plane may be limited, giving rise to micelle-like objects that are spherical or cylindrical in their overall shape. This conclusion was verified by Hu and coworkers<sup>41</sup> who used Monte Carlo simulations to examine the importance of the non-crystallizable block on crystal growth in micelle formation. They demonstrated a confinement effect of the coils of the non-crystallizable block on the lateral surfaces of lamellar crystals due to their overcrowding on the fold end surfaces.

The reduced tethered chain density  $\hat{\sigma} = \sigma \pi R_g^2$  is a useful concept to understand how corona chain density impacts the conformation of the corona chains and the morphology of the crystal.<sup>42</sup> Here  $\sigma$  is the surface density of the corona chains, equal to the reciprocal of the average area occupied per corona chain, and  $R_g$  is the radius of gyration of the corona chain. The value of  $\hat{\sigma}$  can be interpreted as the number of corona chains attached to an area corresponding to the dilute solution radius of gyration of the corona chain. Zheng et al.<sup>43</sup> have shown for single crystals of PEO-*b*-PS and PLLA-*b*-PS that very high values of  $\hat{\sigma}$  (up to 24), can be reached without disrupting the planar geometry of the system. These values are not only indicative of strong corona repulsion and the highly stretched brush regime of the corona chains. They also indicate that the crystal packing forces are sufficiently strong to resist disruption by the strong overlap of the corona chains.

In contrast, the morphology of colloidal aggregates of PCL-*b*-PEO in water seems much more sensitive to factors that affect the swelling or contraction of the corona chains. In these aggregates, PCL forms the crystalline core and PEO forms the water-swollen corona. Under many sample preparation conditions and for a variety of different block ratios, multiple morphologies are observed.<sup>28</sup> One study of PCL-*b*-PEO showed that exposure of spherical micelles in water to high ionic strength led to a morphological transition to lower curvature

structures such as rods and lamellae.<sup>26</sup> The authors explained that ionic strength promotes contraction of the PEO chains due to salting-out, and in this way induced the change in morphology. A similar sphere-to-cylinder transformation was observed for aqueous micelles of PCL<sub>66</sub>-*b*-PEO<sub>44</sub> upon addition of base. At low pH, the mean dimensions of PEO also contract, due to a decrease in hydrogen bonding between the PEO and water.<sup>25</sup> More recently, the groups of Xu and Du<sup>44</sup> report that addition of phenol to a solution of rod-like micelles of PCL<sub>59</sub>-*b*-PEO<sub>113</sub> in water led to their fragmentation into shorter structures whereas addition of threonine to the short structures promoted their reassembly into longer rod-like micelles. This effect was explained in terms of the hydrogen bonding between phenol and PEO, which led to swelling of the chain dimensions, as opposed to the multiple hydrogen bonds between threonine and PEO, which promoted contraction of the chain dimensions.

For many years, our group has been interested in CDSA of block copolymers with PFS as the crystalline core-forming block.<sup>11,45</sup> Rod-like micelles are formed when the corona-forming block is longer than the PFS block. One of the remarkable features of PFS block copolymer micelles is that they undergo seeded growth. If one adds a solution of unimer (molecularly dissolved block copolymer) in a good solvent to a solution of rod-like PFS block copolymer micelles in a selective solvent, the new polymer adds to the ends of the micelles in an epitaxial growth process.<sup>12</sup> In this way, elongated structures, block comicelles, and more complex structures can be formed.<sup>12,46-51</sup> Our interest in PFS is related to the great potential of this polymer for creating and controlling exceptional hierarchical micellar architectures<sup>46,48,51</sup> as well as hybrid structures involving inorganic building blocks.<sup>47,52,</sup>

PFS block copolymers with poly(2-vinylpyridine) (P2VP) as the corona forming block, sometimes exhibits more complex behavior than PFS block copolymers with non-polar corona chains. For example PFS<sub>17</sub>-*b*-P2VP<sub>170</sub> forms spherical micelles in methanol and rod-like micelles in 2-propanol (2-PrOH),<sup>53</sup> whereas PFS<sub>23</sub>-*b*-P2VP<sub>230</sub> forms mixtures of spheres and rods in ethanol that evolve over time.<sup>38</sup> Another sample with a short PFS core-forming block and a P2VP block comparable in length (PFS<sub>74</sub>-*b*-P2VP<sub>74</sub>) formed spherical micelles in THF/2-PrOH mixtures that evolved into lenticular platelet structures.<sup>54</sup> In contrast, PFS<sub>102</sub>-*b*-P2VP<sub>625</sub>, with a long PFS block, formed mixtures of rod-like and spherical micelles in alcohol solvents,<sup>55</sup> while PFS<sub>44</sub>-*b*-P2VP<sub>264</sub> with a shorter PFS block but the same block ratio formed exclusively rigid rod micelles.<sup>56</sup> To summarize, the morphology of PFS-*b*-P2VP in alcohol solvents is sensitive to many parameters such as the block ratio, length of the PFS block, solvent composition and sample preparation conditions.

The variability of PFS-*b*-P2VP self-assembly in alcohol solvents suggests that factors that affect the corona, such as the reduced tethering density, might influence the morphology of the system, as described above for self-assembled structures formed by PCL-*b*-PEO. In the experiments described here, we explore a different variable and examine how a slight chemical modification of the corona-forming block of three different PFS-*b*-P2VP block copolymers (PFS<sub>17</sub>-*b*-P2VP<sub>170</sub>, PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub>) affects their self-assembly in 2-PrOH. We subjected the P2VP block in PFS-*b*-P2VP micelles in 2-PrOH to a small extent of quaternization using methyl iodide, which results in a small number of pyridinium ions along the backbone. We refer to these polymers as PFS-*b*-P2VP<sup>Q</sup>. After removing the excess methyl iodide and drying of these samples, we examined the structures obtained in 2-PrOH by a heating-cooling self-assembly protocol. Although the degree of quaternization is only on the order of a

few mole percent, the presence of these modified sites has a profound effect on the nature of the self-assembled structures formed. We then used the objects obtained as templates for seeded growth. In this way, we were not only able to generate uniform structures of considerable complexity, but we were able to examine which edges of these structures were active at nucleating further growth. The structures obtained were prepared via a one-pot self-assembly protocol.

## EXPERIMENTAL

### *Materials*

The synthesis and characterization of the PFS-*b*-P2VP block copolymers samples examined here (PFS<sub>17</sub>-*b*-P2VP<sub>170</sub>, PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub>) have been described in previous publications.<sup>53,55</sup>

### *Instrumentation*

**<sup>1</sup>H NMR.** <sup>1</sup>H NMR spectra were recorded in dimethyl sulfoxide (DMSO) on a 700 MHz Varian spectrometer at 25 °C. Acquisition parameters included 1024 transients and a  $t_1$  delay of 10 seconds.

**Transmission Electron Microscopy (TEM).** TEM images were obtained using a Hitachi H-7000 transmission electron microscope operating at 100 kV. A 10  $\mu$ L drop of the micelle solution was placed on a Formvar/carbon-coated copper grid and then most of the liquid on the grid was absorbed by touching the edge of the drop with a filter paper. In the study of the dimension of the different micelles, we analyzed the lengths of the micelles ( $L$ ) and their mean width ( $w$ ). For more complex aggregate-structures, we analyzed the width of the central platelet, number average length ( $L_n$ ) and mean width ( $d_f$ ) of the protruding fibers. These values are



collected in Table S1, Supporting Information. Mean length and width values were calculated after measuring at least 100 different positions on several micelles and analyzing them using the software program ImageJ from the National Institutes of Health.

**Atomic force microscopy (AFM).** AFM measurements were carried out with a Digital Instruments, Dimension 5000, Nanoscope IIIa instrument using the same samples prepared for TEM. High resonance frequency silicon probes with a spring constant of  $42 \text{ N m}^{-1}$ , and resonance frequency of  $\sim 320 \text{ kHz}$ , (NanoWorld, Switzerland) were used for tapping-mode imaging in air. The scan rate was 1 Hz and the collected images were  $512 \text{ pixels} \times 512 \text{ pixels}$ . Height and phase images were analysed by the Nanoscope V1.40 software.

#### ***Partial quaternization of PFS-*b*-P2VP copolymers***

The partially quaternized PFS-*b*-P2VP copolymers (PFS-*b*-P2VP<sup>Q</sup>) were prepared following a protocol similar to that described previously.<sup>57</sup> Briefly, micelles of PFS-*b*-P2VP were prepared by heating a sample of PFS-*b*-P2VP (5 mg) in 2-PrOH (10 mL) at 90 °C for 30 minutes, after which the sample was removed from the bath and allowed to cool to room temperature and age for one day. In the case of PFS<sub>36</sub>-*b*-P2VP<sub>502</sub>, the polymer was heated in a mixture of THF (500  $\mu\text{L}$ ) and 2-PrOH (10 mL) to increase the solubility of the block copolymer in the hot solution followed by cooling and aging. CH<sub>3</sub>I was then added to the solutions of the micelles in 2-PrOH in a mole ratio of 5:1 CH<sub>3</sub>I/pyridine group. Different extents of quaternization of P2VP were obtained by varying the reaction time. The reaction was quenched by adding an excess of hexanes (20  $\times$  by volume) to precipitate the micelles, and the block copolymer micelles were purified from unreacted CH<sub>3</sub>I by three cycles of redispersion in 2-PrOH followed by precipitation with hexanes. The final product was dried in a vacuum oven at room temperature for 24 h. The powder was using as it is for the self-assembly procedure.

The overall degree of quaternization of the polymers was evaluated by  $^1\text{H}$  NMR (in DMSO- $d_6$ ) by comparing the integration of the  $\alpha$ -proton signal in the pyridinium units at 8.7 ppm to the  $\alpha$ -proton signal in the pyridine units at 8.2 ppm (Figure S1). The mole percent of quaternization and the mean number of pyridinium units per chain in three quaternized PFS-*b*-P2VP copolymers (PFS-*b*-P2VP<sup>Q</sup>) are shown in Table 1.

**Table 1.** Nomenclature, degree of quaternization and number of charges per polymer for the different block copolymers used.

| Block copolymer  | Degree of quaternization <sup>a</sup> | -C <sub>5</sub> H <sub>5</sub> N-CH <sub>3</sub> (+) per polymer <sup>b</sup> |
|--|---------------------------------------|---|
| PFS <sub>17</sub> - <i>b</i> -P2VP <sub>170</sub> <sup>Q0.1%</sup> | 0.1%                                  | 1   |
| PFS <sub>17</sub> - <i>b</i> -P2VP <sub>170</sub> <sup>Q3%</sup>   | 3%                                    | 5   |
| PFS <sub>30</sub> - <i>b</i> -P2VP <sub>300</sub> <sup>Q3%</sup>   | 3%                                    | 9   |
| PFS <sub>30</sub> - <i>b</i> -P2VP <sub>300</sub> <sup>Q6%</sup>   | 6%                                    | 18  |
| PFS <sub>36</sub> - <i>b</i> -P2VP <sub>502</sub> <sup>Q1%</sup>   | 1%                                    | 5   |
| PFS <sub>36</sub> - <i>b</i> -P2VP <sub>502</sub> <sup>Q3%</sup>   | 3%                                    | 15  |

- a. Mole percent of methylpyridinium groups per polymer determined by  $^1\text{H}$  NMR by comparing the integration  $\alpha$ -proton signal in the pyridinium units at 8.7 ppm to the  $\alpha$ -proton signal in the pyridine units at 8.2 ppm.
- b. Mean number of methylpyridinium groups per polymer.

### ***Self-assembly of PFS-*b*-P2VP and PFS-*b*-P2VP<sup>Q</sup> copolymers in 2-PrOH***

To prepare fiber-like micelles of the non-quaternized PFS<sub>17</sub>-*b*-P2VP<sub>170</sub> and PFS<sub>30</sub>-*b*-P2VP<sub>300</sub>, 0.5 mg samples were suspended in 2-PrOH (1.0 mL) in a 3.5 mL vial and then heated at 90 °C

for 30 min, forming clear solutions. These solutions were removed from the oil bath and allowed to cool at room temperature (23 °C) and age for 24 h before an aliquot of solution was taken for TEM analysis. For PFS<sub>36</sub>-*b*-P2VP<sub>502</sub>, this protocol led to a mixture of amorphous material in addition to long micelles. Better defined micelles were obtained with 5 vol % THF in the 2-PrOH. For the corresponding PFS-*b*-P2VP<sup>Q</sup> samples, 0.5 mg aliquots in 2-PrOH (1.0 mL) were heated to 90 °C as described above, cooled to room temperature and allowed to age for 24 h.

### *Seeded growth from the partially quaternized micelles as seeds*

To the three micelle solutions in 2-PrOH containing the highest degree of quaternization, PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q6%</sup>, PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q3%</sup> and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q3%</sup> (each 0.05 mg/0.1 mL), a THF solution of non-quaternized copolymers (PFS<sub>30</sub>-*b*-P2VP<sub>300</sub>, PFS<sub>17</sub>-*b*-P2VP<sub>170</sub> and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub>) (2 µL, 10 mg/mL) was added to its corresponding polymer seed solution. After slight swirling, the solutions were aged for 24 h before TEM analysis.

## **RESULTS**

The non-quaternized block copolymer samples that we examine here (PFS<sub>36</sub>-*b*-P2VP<sub>502</sub>, PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> and PFS<sub>17</sub>-*b*-P2VP<sub>170</sub>) all form elongated fiber-like micelles of uniform width in 2-PrOH. For the last two samples (PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> and PFS<sub>17</sub>-*b*-P2VP<sub>170</sub>), micelles formed when the polymers suspended in 2-PrOH were heated for 30 min at 90 °C and then allowed to cool to room temperature (23 °C) and age for 24 h. For PFS<sub>36</sub>-*b*-P2VP<sub>502</sub>, micelle formation required a solvent containing 5 vol % THF to enhance the solubility of the polymer in the hot solvent. TEM images of examples of these micelles are presented in Figure S2.

Samples of PFS-*b*-P2VP were partially quaternized by treating micelle solutions in 2-PrOH with an excess of methyl iodide at room temperature and varying the amount of time that the

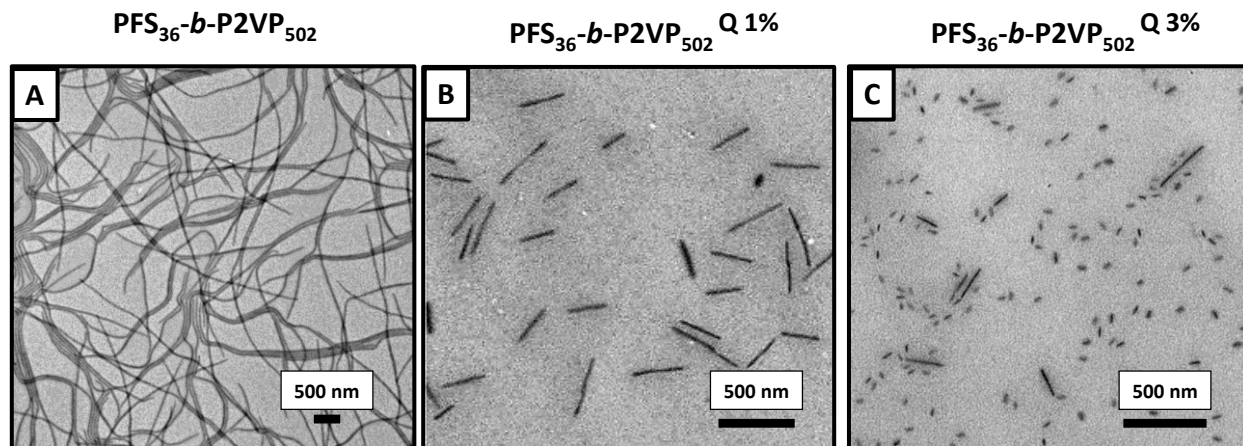
mixture was allowed to react. Experiments showed that extensive methylation resulted in a block copolymer sample that could not be dissolved in hot 2-PrOH. Our intent here was to keep the degree of methylation small enough that the partially quaternized block copolymer would remain sufficiently soluble in hot 2-PrOH to permit self-assembly by the heating and cooling protocol used for the non-quaternized polymer. After the quaternization reaction, the micelles were precipitated with hexane to quench the reaction, with the idea that the unreacted methyl iodide would remain in the hexane solution. We recognize that by carrying out the reaction on micelles, the sites of methylation may not be randomly distributed along the P2VP backbone. As shown in Table 1, 6% of the pyridine groups were quaternized in one polymer sample (PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q6%</sup>) whereas other samples had lower degrees of quaternization.

### ***Comparison of the self-assembly of PFS-*b*-P2VP and PFS-*b*-P2VP<sup>Q</sup>***

In this section, we compare the self-assembly of the three different PFS-*b*-P2VP block copolymers prior to quaternization with that of the block copolymers partially quaternized with methyl iodide.

**Self-assembly of PFS<sub>36</sub>-*b*-P2VP<sub>502</sub> and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q</sup>.** In Figure 1 we present TEM images of PFS<sub>36</sub>-*b*-P2VP<sub>502</sub> (Figure 1A), PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q1%</sup> (Figure 1B) and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q3%</sup> (Figure 1C). Figure 1A shows that PFS<sub>36</sub>-*b*-P2VP<sub>502</sub> formed long uniform fiber-like micelles with a cross section width  $d_f = 47$  nm. While their lengths are difficult to measure, we estimate them to be on the order of 5  $\mu$ m. For this polymer, the two partially quaternized samples contained an average 1% (5 per chain) and 3% (15 per chain) methylpyridinium units. For both for PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q1%</sup> and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q3%</sup> we found short rod-like structures, rather polydisperse in length (Figures 1B and 1C, respectively). The sample with the smaller extent of methylation showed longer and slightly wider micelles (number average length  $L_n = 250$  nm and

width  $d_f = 44$  nm) than the  $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}^{\text{Q3\%}}$  sample ( $L_n = 50$  nm and  $d_f = 16$  nm). For the Q3% sample, there appears to be a mixture of longer micelles and shorter stubby structures.



**Figure 1.** TEM images of the micelles formed by (A)  $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}$ , (B)  $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}^{\text{Q1\%}}$  and (C)  $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}^{\text{Q3\%}}$ . The initial micelle sample in A was obtained by heating the block copolymer in 2-PrOH containing 5% THF to 90°C followed by cooling and aging 24 h at room temperature. After partial quaternization, the samples in B and C were obtained by a similar heating, cooling and aging protocol in 2-PrOH.

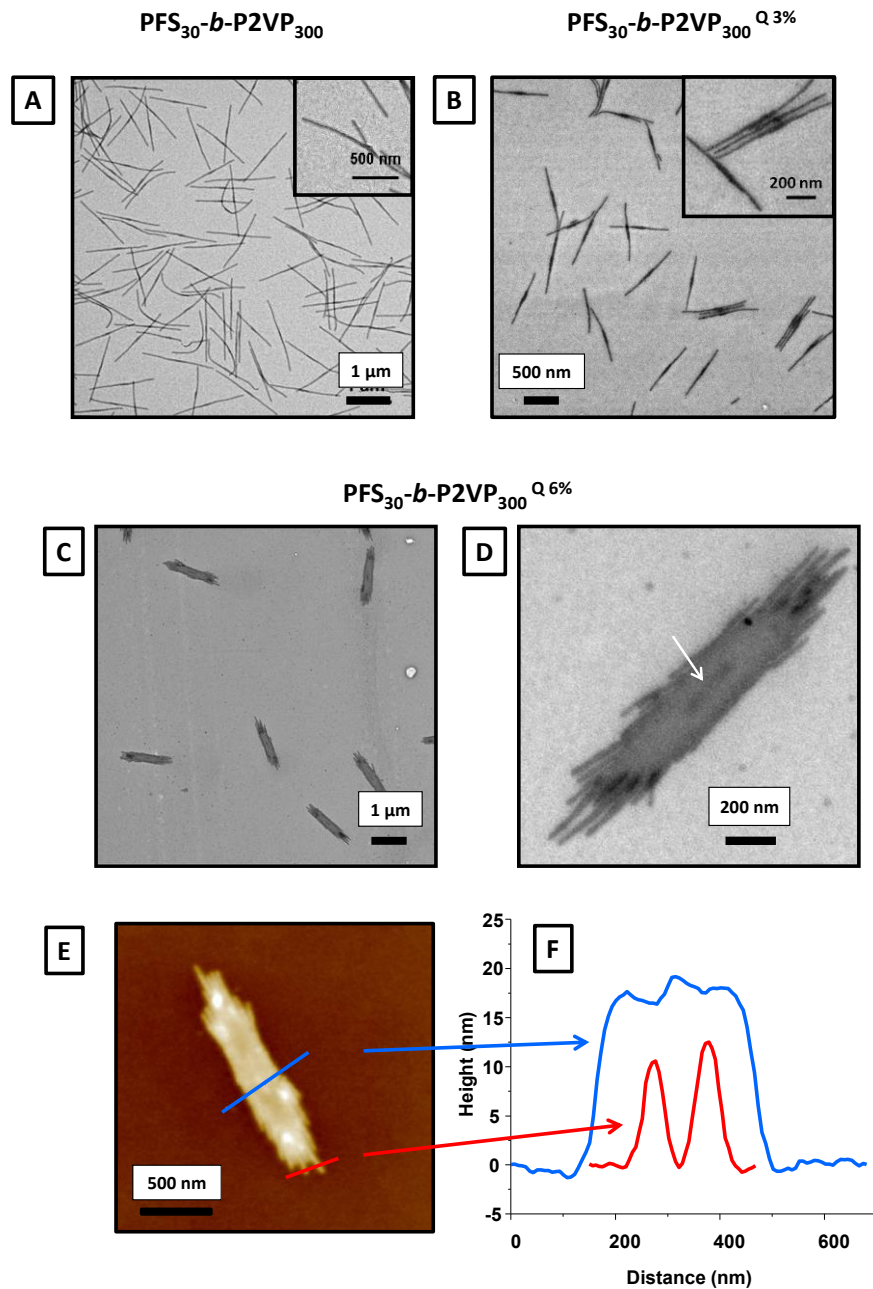
We assume that the reduced solvent quality for the partially quaternized corona chains makes the block copolymers more resistant to complete dissolution in the heating-cooling cycle process. If nucleation for these samples is enhanced, then more nuclei will form when the degree of quaternization is increased, leading to a larger number of shorter micelles. We were concerned that the short length of these micelles might indicate poisoning of their growth. To examine this possibility, we treated a suspension of these  $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}^{\text{Q3\%}}$  micelles (0.05 mg) in 0.1 mL 2-PrOH with unimer of  $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}$  (2  $\mu\text{L}$ , 10 mg/mL) in THF. The small amount of  $\text{PFS}_{36}\text{-}b\text{-P2VP}_{502}$  added to the sample grew epitaxially off the ends of these micelles, making them somewhat longer (Figure S3). This seeded growth experiment establishes that the ends of the micelles remain active toward further deposition of block copolymer. We have more to say about seeded growth experiments with the other block copolymer samples later in the paper.

We also considered the possibility that fragmentation during the quaternization process was responsible for the short micelles seen in Figure 1C. We carried out a control experiment to test whether fragmentation occurred during the methylation reaction. We repeated the reaction of PFS<sub>36</sub>-*b*-P2VP<sub>502</sub> micelles with methyl iodide to form PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q3%</sup>, carefully comparing the TEM of the reaction product with that of the starting micelle sample. While both the initial sample and the final reaction product consisted of micelles with lengths that were too long to measure directly, Figure S4 shows that there are no obvious differences between the two images. We can conclude that neither the methylation reaction nor the 12 h stirring of the reaction mixture led to significant fragmentation of the micelles.

These experiments establish that small amounts of quaternization and different degrees of quaternization of the P2VP chains of PFS<sub>36</sub>-*b*-P2VP<sub>502</sub> influence the self-assembly of the block copolymer in 2-PrOH. Based on these results, we wanted to investigate and understand how the length of the corona and the number of charges will affect the self-assembly process of other PFS-*b*-P2VP block copolymers. In the next two sections we describe the self-assembly behavior of two samples that have similar block ratios but smaller coil and crystalline blocks (PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> and PFS<sub>17</sub>-*b*-P2VP<sub>170</sub>).

**Self-assembly of PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> and PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q</sup>.** Heating samples of PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> in 2-PrOH and cooling led to long uniform fiber-like micelles characterized by  $d_f = 35$  nm (Figure 2A). Figures 2B, 2C and 2D present the TEM images of micelles formed by partially methylated polymer (PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q</sup>). Here the two quaternized samples carried an average of 3 mol % (9 per chain) and 6 mol % (18 per chain) methylpyridinium groups. Figure 2B shows that PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q3%</sup> formed long, thin structures (~ca. 800 nm long) with a wider part in the center (Figure 2B and Figure S5). These micelles were relatively uniform in length, but a

significant fraction of the micelles appeared to have become joined in the wider middle section. The morphology changed in a more substantial way when we carried out self-assembly of the sample with 6 mol % quaternization ( $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q6\%}}$ ). Here we found platelet-like shapes of similar size with fibers protruding from the ends and to some extent from the sides (Figure 2C and 2D and Figure S6). These objects resemble the “fringed raft-like” structures reported by van de Ven and Eisenberg<sup>59</sup> for blends of  $\text{PCL}_{24}\text{-}b\text{-PEO}_{45}$  + 10 wt %  $\text{PCL}_{10}$  homopolymer in water. The  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q6\%}}$  micelles are about a factor of two longer than the  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q3\%}}$  micelles. Interestingly, higher magnification TEM images show a small dark line in the center of the micelle (white arrow, Figure 2D). These  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q6\%}}$  structures were further characterized by AFM, as shown in Figures 2E and 2F. The line across the center of micelle shows a relatively flat platelet-like structure approximately 18 nm high. The fibers at the ends of the structure are half of the height of the central platelet. The central core, which seems darker than the rest of the micelle in the TEM images, is approximately 3 nm higher than the platelet itself. Additional AFM images of the  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q6\%}}$  micelles are presented in Figures S7.

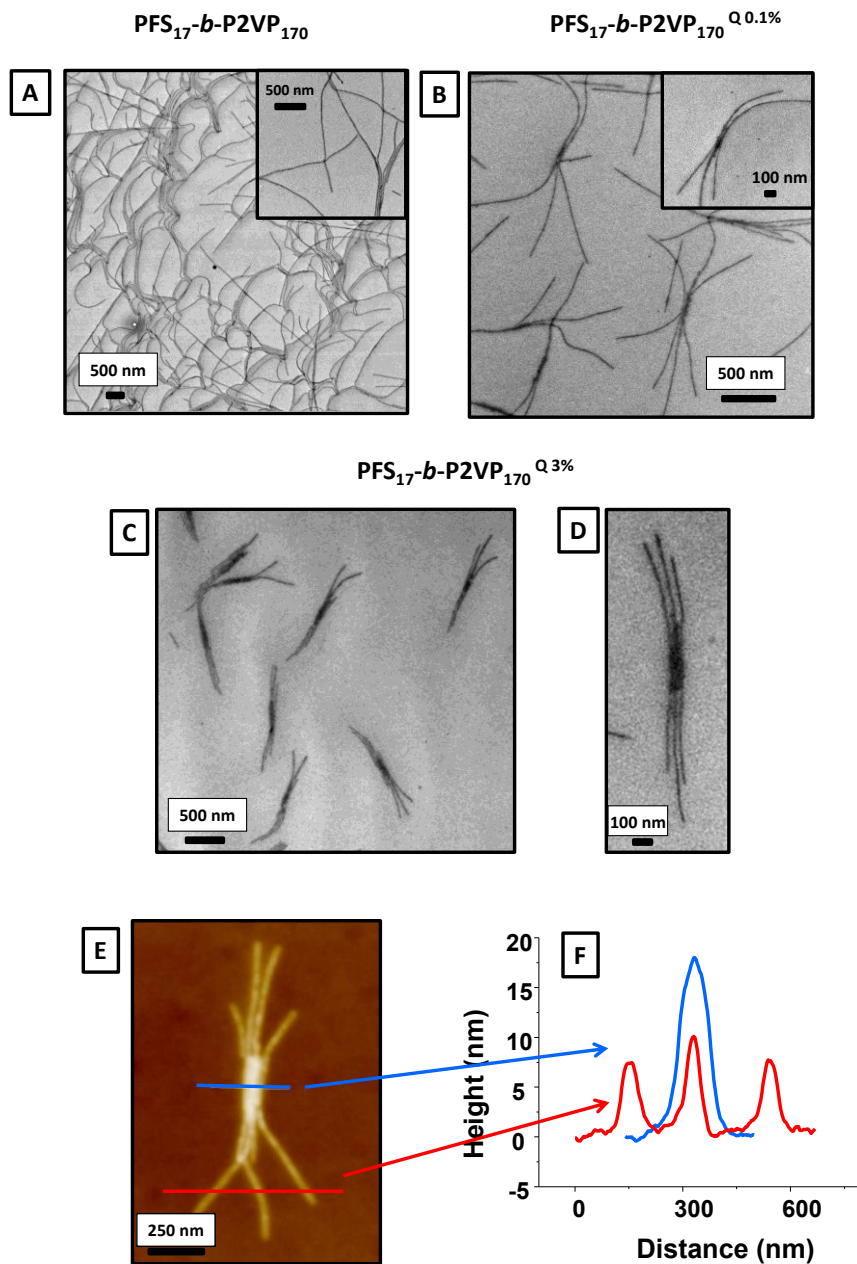


**Figure 2.** TEM images of micelles of (A)  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}$ , (B)  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q}3\%}$ , (C) and (D)  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q}6\%}$  formed in 2-PrOH prepared by heating the mixture in an oil bath at 90  $^{\circ}\text{C}$  followed by cooling and aging 24 h at room temperature. Figure (E) AFM height image of  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q}6\%}$ . Figure (F) shows the section analysis of the structure in E along the blue and red lines.



**Self-assembly of PFS<sub>17</sub>-*b*-P2VP<sub>170</sub> and PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q</sup>.** This block copolymer, upon heating and cooling in 2-PrOH, formed long fiber-like micelles of uniform width. By TEM, we determined a mean width of 35 nm. This diameter is larger than the core diameter of 10 nm reported for PFS<sub>20</sub>-*b*-P2VP<sub>140</sub> in ref 60 and suggests that in our TEM images the P2VP corona contributes to the micelle width. The micelles are very long (typically  $L > 4 \mu\text{m}$ ), preventing us for obtaining the length distribution. Figure 3B, 3C and 3D present the TEM images for the PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q</sup>. These images show that even a tiny extent of quaternization affects the nature of the self-assembled structures formed. For example, as shown in Figure 3B, PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q0.1%</sup> only formed spider-like structures under these conditions (more examples are presented in Figure S8). The spiders appear to have a narrow central platelet with uniform fiber-like legs protruding from the front and back of the platelet. As indicated in Table 1, these polymers have an average of only 1 pyridinium ion per P2VP chain. Nevertheless, there is a clear change in the type of structures formed.

At a higher degree of quaternization (PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q3%</sup>, Figure 3C, 3D and Figure S9), one also sees uniform spider-like structures, but the body is wider and the “legs” are shorter. The width of the fiber-like legs of these structures decreases also with the quaternization increases (Table S1). An AFM image of one of these structures is presented in Figure 3E (see also Figure S10), with line traces of the object’s height presented in Figure 3F. While the fiber-like legs are approximately 8-10 nm in height, the body itself is twice that height.



**Figure 3.** TEM images of the micelles of (A) PFS<sub>17</sub>-*b*-P2VP<sub>170</sub>, (B) PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q0.1%</sup>, (C) and (D) PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q3%</sup> formed in 2-PrOH. (E) AFM height image of PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q3%</sup> in 2-PrOH. (F) Analysis of the structure in D along the blue and red lines. Samples were prepared by heating polymer solutions in 2-PrOH (0.5 mg/mL) in an oil bath at 90 °C for 30 min followed by cooling in air and aging 24 h.

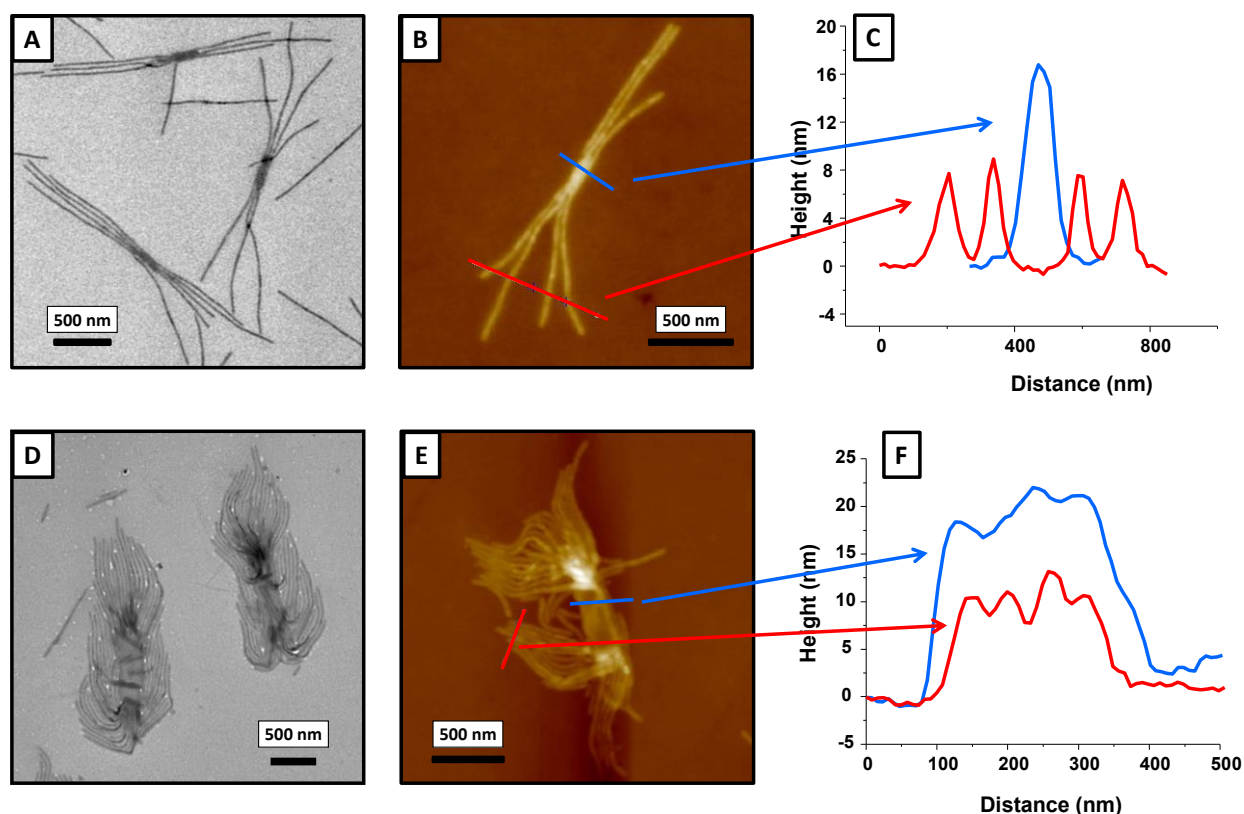
### *Seeded growth*

We next wanted to examine whether the structures formed by the partially quaternized block copolymers could be used as platform for creating hierarchical micellar architectures through CDSA. To proceed, we prepared separate micelle solutions of  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q6\%}}$  and  $\text{PFS}_{17}\text{-}b\text{-P2VP}_{170}^{\text{Q3\%}}$  in 2-PrOH (each 0.05 mg/0.1 mL) and used these structures as templates for seeded growth. To each micelle solution we added a constant amount (2  $\mu\text{L}$ , 10 mg/mL) of the corresponding non-quaternized copolymers ( $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}$  and  $\text{PFS}_{17}\text{-}b\text{-P2VP}_{170}$ , respectively). After the mixtures were aged at room temperature for 24 h, they were examined by TEM and AFM

Figures 4 A-C show the results for adding  $\text{PFS}_{17}\text{-}b\text{-P2VP}_{170}$  to  $\text{PFS}_{17}\text{-}b\text{-P2VP}_{170}^{\text{Q3\%}}$  seeds (more examples are shown in Figure S11 A, B). The legs of the spiders have grown longer, a signature of seeded growth. In addition, one can find a few isolated rod-like micelles in the TEM images. These may be spider legs that have broken off the bodies as the sample dried on the grid, rather than independently generated micelles, that likely would have been much longer. It is important to note that we do not observe any change in the width of the new elongated micelles or new legs growing elsewhere off the body. The AFM image in Figure 4B and the section analysis presented in Figure 4C show that the legs and body preserve the heights seen for the original structures (more AFM images and their analysis is presented in Figure S12 A, B). Thus the newly added polymer appears to have deposited and grown only off the legs of the original structures. There was no evidence that micelles nucleated off the planar body of the spider-like templates.

Figures 4 D-F (and Figure S11 C,D) show corresponding results for adding  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}$  in THF to  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q6\%}}$  seeds in 2-PrOH. The seed templates themselves (Figures 2 C,D)

are characterized by a larger central body (up to 2  $\mu\text{m}$  in length) with many short stubby protruding legs. After addition of  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}$  in THF, the legs grow much longer, and the central body is surrounded by these fiber-like structures. Here, too, the AFM images and the sector analysis (Figures 4 E,F, Figure S12) show that height of the structures did not change significantly during the seeded growth.



**Figure 4.** (A) TEM image of multi-armed structures formed by the seeded growth by adding  $\text{PFS}_{17}\text{-}b\text{-P2VP}_{170}$  (0.02 mg in 2  $\mu\text{L}$  THF) to platelet-like  $\text{PFS}_{17}\text{-}b\text{-P2VP}_{170}^{\text{Q3\%}}$  seeds (0.05 mg) in 0.1 mL 2-PrOH. (B) AFM height image of one of these structures formed by seeded growth from  $\text{PFS}_{17}\text{-}b\text{-P2VP}_{170}^{\text{Q3\%}}$  (C) section analysis of the structure in B along the blue and red lines. (D) TEM image of multi-armed structures formed by seeded growth by adding  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}$  (0.02 mg in 2  $\mu\text{L}$  THF) to platelet-like  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q6\%}}$  micelles (0.05 mg) in 0.1 mL 2-PrOH. (E) AFM height image of one of these structures formed by seeded growth from  $\text{PFS}_{30}\text{-}b\text{-P2VP}_{300}^{\text{Q6\%}}$  (F) section analysis of the structure in D along the blue and red lines.

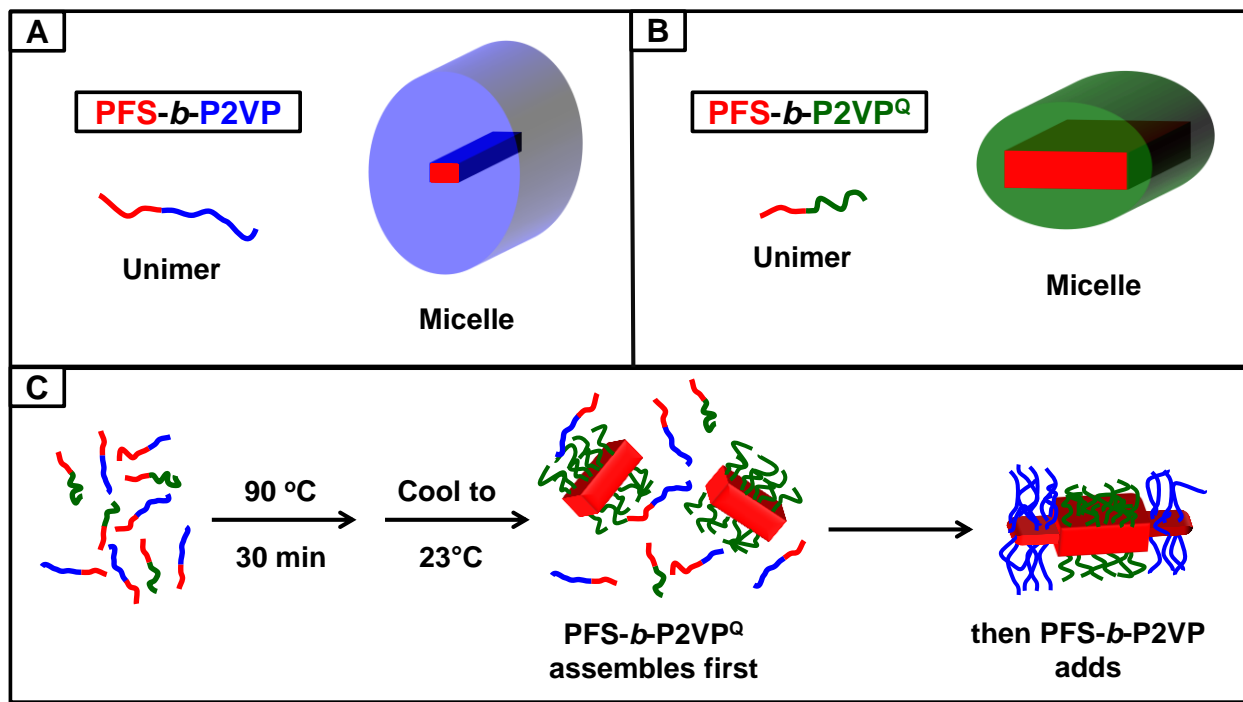
## DISCUSSION

Quaternization of the P2VP block, even small extents of quaternization, changes the nature of the structures formed by the self-assembly of PFS-*b*-P2VP in 2-PrOH. To explain these differences, we begin with the idea that there is a distribution of the extent of methylation of the PFS-*b*-P2VP block copolymer molecules in each sample, and at these low levels of methylation, some of the polymers remain unmodified. We observe that 2-PrOH is a poorer solvent for the polymer containing N-methyl-pyridinium groups than for P2VP itself. From this perspective, PFS-*b*-P2VP<sup>Q</sup> chains would be the first in the sample to aggregate and self-assemble by crystallization of their PFS blocks. In this way, we explain the formation of the plate-like portion of the self-assembled structures, and we believe that these domains are enriched in the polymer with the highest extent of quaternization. The types of morphologies that we observe are different than those found by a change of solvent. A change in solvent polarity, for example, would have a global effect on all of the corona chains. In contrast, the quaternization of the pyridine groups has only a local effect on the conformation of the corona chains. Once the polymer chains with the highest degree of quaternization have been consumed, more of the less quaternized PFS-*b*-P2VP will be incorporated in the micelles. Non-quaternized PFS-*b*-P2VP polymers will have a much stronger tendency to form fiber-like micelles. These fiber-like micelles grow preferentially from narrow ends of the elongated planar centers. For each extent of quaternization, the structures formed exhibit a remarkable uniformity.

We would like to emphasize that because 2-PrOH is a poorer solvent for P2VP<sup>Q</sup> than for P2VP, the P2VP<sup>Q</sup> corona chains will be less swollen by solvent than P2VP polymer chains. The decrease in the corona dimensions should lead to an increase in the tethering density of the corona chains, which would favor a decrease in the number of folds in the PFS core-forming

chains and a thicker core than in the fiber-like micelles formed by the unquaternized polymer.

Figure 5 illustrates this process of micelle formation.



**Figure 5.** A), B) In the individual unimers, the red color represents the PFS crystalline-core-forming block. Blue represents the corona-forming P2VP block. Green indicates the partially quaternized P2VP block (P2VP<sup>Q</sup>). In the micelle structures, red represents the PFS core; and blue and green represent the overall shape of their respective micelle coronas. (C) Schematic representation of the formation of micelles for PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q</sup> and PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q</sup>. As the solution cools, the polymer molecules with the highest degree of quaternization assemble first to form a platelet core, followed by deposition on the ends of the platelets of molecules with fewer pyridinium groups that tend to form narrower cylindrical structures.

For both PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q</sup> samples we obtained multi-armed micelles with a thin central platelet and note that no fibers grew perpendicular to, or protruded from, the sides of the platelets. Instead, the fibers grew as tassels from both ends of the long-axis of the central part. The structures thus resembled scarf-like micelles formed from the addition of PFS<sub>57</sub>-*b*-PI<sub>342</sub> unimers to elongated platelet micelles of PFS<sub>76</sub>-*b*-PI<sub>76</sub>.<sup>61</sup> From the analysis of multiple TEM images of the multi-armed PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q</sup> micelles, we determined the characteristic lengths and widths of both the central platelet and the protruding tassels. We summarize these results in

Table S1. The central platelet became wider and longer with higher degrees of quaternization. The length and the width of the protruding fibers also decreased as the extent of methylation of the polymer increased. In Figure S13 we compare the number of fiber-like tassels attached to each end of the central platelet. For PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q0.1%</sup>, most of the micelles had two tassels (2:2) (“m:n” designates that a micelle has “m” branches at one end and “n” branches at the other end attached to each end). Some had one tassel at one end and two tassels at the other end (1:2), and some had 3:3. For PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q3%</sup>, most of the micelles were 2:2, 2:3, 3:3 and 3:4. A smaller fraction of micelles had 4 or 5 tassels at one end.

These structures are consistent with our hypothesis about the initial formation of a planar core that serves as a seed to nucleate the growth of elongated fibers (c.f., Figure 5). Quaternization can affect the length of the tassels at the ends of the central platelet in two ways. First, at higher levels of quaternization, a larger fraction of the sample becomes part of the central platelet, leaving less fiber-forming block copolymer to be incorporated into the tassels. Second, a wider central platelet will provide more sites for seeded growth of the fiber-like structures, primarily formed by non-quaternized polymers. This leads to the formation of more fibers that are on average shorter in length.

To put our findings in context, we briefly return to other examples of PFS block copolymers with a polar corona-forming block where branched or lenticular micelles have been observed. Qiu et al.<sup>60</sup> found that the core cross section of several fiber-like PFS-*b*-P2VP micelles formed in 2-PrOH increased with the length of the PFS block. They prepared micelles of PFS<sub>48</sub>-*b*-P2VP<sub>414</sub> and used these as seed for the growth of much thinner PFS<sub>20</sub>-*b*-P2VP<sub>140</sub> micelles. In this way, two or even three of the thinner micelles grew from the ends of the wider micelle seeds. Yusoff et al.<sup>54</sup> examined micelle formation of PFS<sub>74</sub>-*b*-P2VP<sub>74</sub> in 2-PrOH-rich solvent media. This

polymer, because of its short corona-forming block might be expected to form planar micelles. These authors found that the structure of the objects formed depended sensitively on the self-assembly protocol. By adding THF to a suspension of the polymer in 2-PrOH, they obtained elongated planar objects with two or three fibers protruding from the ends which the authors described as “aggregated lenticular platelet micelles”. An AFM image of one of these objects (see Fig 3b,c in ref 54) resembles the structure we present in Fig 3E,F above, with a central core (height ~19 nm) not quite twice as thick as the fiber-like protrusions (height ~10 – 12 nm) at the ends. These authors propose that the aggregates arise by the formation of platelet nuclei in the nucleation step and then subsequently grow into the observed nanostructures over time.<sup>54</sup>

A more obvious example where a seed micelle acts as a nucleus for the formation of a lenticular structure is found in the work of Soto et al.<sup>62</sup> These authors generated uniform pointed oval-shaped planar micelles from PFS<sub>54</sub>-*b*-PP<sub>290</sub> (PP, poly[bis(trifluoroethoxy)-phosphazene]) when this polymer as a solution in THF was added to a suspension of rod-like PFS-*b*-P2VP micelles in 2-PrOH. The PFS<sub>54</sub>-*b*-PP<sub>290</sub> itself did not give well-defined colloidal objects in this solvent, whereas in the presence of the PFS<sub>34</sub>-*b*-P2VP<sub>272</sub> seed micelles, the PFS block of the newly added polymer appeared to add to the sides and to the ends of the seeds to form planar oval-shaped structures. The authors of this paper also explored the use of the pointed-oval-shaped micelles as precursors to hierarchical micelle architectures through crystallization-driven self-assembly. They added small amounts of PFS<sub>34</sub>-*b*-P2VP<sub>272</sub> as solution in THF to a suspension of the pointed oval objects in 2-PrOH. In this way they generated short rod-like structures from the ends of the ovals, and the TEM images obtained (Fig 3a in ref 62) also resemble the structures obtained for PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q6%</sup> shown in Figures 3D and 3E.



What distinguishes our system from previous examples in the literature is that our partially quaternized block copolymers contain a distribution of structures, consisting of a mixture of corona chains. We believe that chemical fractionation played a key role in the self-assembly process.

## SUMMARY AND CONCLUSIONS

In the work described here, we compared the self-assembly in solution of three PFS-*b*-P2VP block copolymers (PFS<sub>17</sub>-*b*-P2VP<sub>170</sub>, PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub>) with that of lightly quaternized derivatives (denoted PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q</sup>, PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q</sup> and PFS<sub>36</sub>-*b*-P2VP<sub>502</sub><sup>Q</sup>) obtained by a reaction with methyl iodide. Under our heating-and-cooling self-assembly protocol in 2-PrOH, all three non-ionic block copolymers formed long fiber-like micelles of uniform width. For the partially quaternized polymers, we found that the morphologies obtained were highly dependent on the amount of charge and the length of the corona block.

We explain the complexity of the structures obtained in terms of a distribution of compositions of polymers lightly quaternized with methyl groups. The polymers with the highest extent of methylation are the least soluble in 2-PrOH, suggesting that these block copolymers are the first to associate. They form planar nuclei that grow by CDSA as more PFS chains deposit epitaxially on these seeds. As the growth proceeds, the polymer remaining in solution is reduced or depleted in its positively charged pyridinium content. These polymers have a strong tendency to form elongated fiber-like micelles that grow from the ends of the initially formed planar structures. The growth of these micelles from the ends of the planar seed structures demonstrates that partial quaternization of the P2VP chains does not poison the edges of the initially formed structures against future growth. To emphasize this point, we carried out seeded growth experiments in which we added solutions of PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> in THF to micelles of PFS<sub>30</sub>-*b*-

P2VP<sub>300</sub><sup>Q</sup> in 2-PrOH, and solutions of PFS<sub>17</sub>-*b*-P2VP<sub>170</sub> in THF to micelles of PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q</sup> in 2-PrOH. In both instances, the newly added polymer grew onto the ends of the fibers protruding from the colloidal aggregates formed by the partially quaternized block copolymer.

The two most important conclusions from our study are (i) that small changes in the corona chemistry led to complex but uniform structures that varied with the extent of corona modification, and (ii) that these complex structures were all obtained in a one-pot self-assembly protocol.

This study opens the door to further studies of core-crystalline block copolymer micelle formation, where small extents of chemical modification of the corona forming chains can modify the self-assembly process, and where simple one-pot protocols can lead to diverse structures.

## ASSOCIATED CONTENT

**Supporting Information.** Analysis of the dimensions of the micelles; NMR spectra of PFS<sub>30</sub>-*b*-P2VP<sub>300</sub>, PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q 3%</sup> and PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q 6%</sup> in DMSO; low and high magnification TEM images of the micelles of the three PFS-*b*-P2VP and all the PFS-*b*-P2VP<sup>Q</sup>; AFM height images and analysis of the AFM structure of PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q 6%</sup> and PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q 3%</sup>; low and high magnification TEM images and AFM height images of the “star” structure formed by the seeded growth method by adding PFS<sub>17</sub>-*b*-P2VP<sub>170</sub> (0.02 mg) to platelet-like PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q 3%</sup> seeds (0.05 mg) in 0.2 mL 2-PrOH; low and high magnification TEM images and AFM height images of the “fish” structures formed by seeded growth method by adding PFS<sub>30</sub>-*b*-P2VP<sub>300</sub> (0.02 mg) to platelet-like PFS<sub>30</sub>-*b*-P2VP<sub>300</sub><sup>Q 6%</sup> seeds (0.05 mg) in 0.2 mL 2-PrOH;

distribution of the number of branches per micelles of PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q0.01%</sup> and PFS<sub>17</sub>-*b*-P2VP<sub>170</sub><sup>Q3%</sup>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Notes:** The authors declare no competing conflict of interest.

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